

APPLICATION FOR PATENT

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TITLE: CATALYST SYSTEM FOR OXIDATIVE
DEHYDROGENATION OF PARAFFINS

SPECIFICATION

FIELD OF THE INVENTION

5 The present invention relates to a catalyst composition for an oxidative dehydrogenation of organic compounds having alkane functionality to organic compounds having alkene functionality. The present invention also relates to a catalytic process for the oxidative dehydrogenation of alkanes to alkenes.

BACKGROUND OF THE INVENTION

10 Unsaturated alkenes are useful as monomers and comonomers for the formation of commercially valuable polymers. The conversion of lower value saturated hydrocarbons into higher value unsaturated hydrocarbons is economically desirable. Oxidative dehydrogenation of saturated hydrocarbons to form unsaturated hydrocarbons has been accomplished using catalysts in high temperature gas phase reactions.

15 Numerous catalysts which can be used for the oxidative dehydrogenation of saturated or paraffinic hydrocarbons have been reported. Mixed nickel and tin oxides have been disclosed in U.S. Patent No. 3,745,194; U.S. Patent No. 3,801,671; and U.S. Patent No. 5,086,032. Complex metal oxide catalyst including vanadium and aluminum for oxidative dehydrogenation of hydrocarbons has been disclosed in U.S. Patent No. 4,046,833.

20 Catalysts, having crystalline structures, useful for the oxidative dehydrogenation of saturated hydrocarbons to form unsaturated hydrocarbons are known. U.S. Pat. No. 5,772,898 discloses a metallo manganese oxide having a hollandite structure and an intracrystalline pore system.

U. S. Pat. No. 4,777, 319 discloses a catalyst for oxidative dehydrogenation of hydrocarbons using metal vanadate compounds which are described as having crystalline structures. U.S. Pat. No. 5,139,988 discloses an iron-antimony containing oxide catalyst in which the iron antimonate is crystalline. U.S. Pat. No. 4,973,793 discloses crystalline catalyst compositions having iron, oxygen and at least one other metallic element. U.S. Patent 4,658,074 also discloses crystalline catalysts having iron, oxygen and at least one other metallic element.

Calcination is commonly used as one step in the process of preparing catalysts useful for oxidative dehydrogenation. U.S. Patent No. 3,860,534 disclosed high temperature calcinations at 700 °C to 900 °C.

A desire still exists in the art to develop catalyst that will promote a high conversion of alkane starting material with high selectivity to an alkene product material of the same carbon number so as to enable the attainment of a high yield of product per pass.

SUMMARY OF THE INVENTION

One embodiment of this invention is a catalyst in an oxide form containing aluminum, vanadium and antimony which is useful for the oxidative dehydrogenation of organic compound having at least two adjacent carbon atoms each having at least one hydrogen atom. The catalyst composition is represented by the formula $A_aB_bSb_cV_dAl_eO_x$ wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present. The catalyst is prepared by a low temperature process with a calcination temperature below about 650 °C. The catalyst is prepared by a process comprising at least a step of heating the catalyst to its calcination temperature using a heating velocity of less than 15 °C/minute. The catalyst is substantially amorphous, i.e. without any long range lattice order. The preferred catalyst compositions promote a high conversion of alkane starting material with high selectivity to alkene product material of the same number of carbon atoms to enable production yields of up to 30% per reactor pass.

to an alkadiene. For example, the process can convert isopentane to isopentene or convert isopentane, through an isopentene intermediate, to isoprene.

CATALYST COMPOSITION

The catalyst composition is represented by the formula $A_aB_bSb_cV_dAl_eO_x$ wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present.

Catalyst precursors may be prepared by conventional physical methods utilizing mixing, co-precipitation, impregnation and filtration. Preferred starting materials are water soluble metal salts which include, but are not limited to, metal nitrates, chloride, oxalates and hydroxides. For metal salts in which the metal is an anionic ion, an ammonium cation may be used as a counterion.

The catalyst of the present invention can be produced by preparing one or more solutions or slurries, preferable aqueous solutions or slurries, each containing one or more of the starting materials. For example, a slurry of an alumina precipitate is formed by adjusting the pH of an aluminum salt solution with ammonium hydroxide. The remaining solutions or slurries are mixed, with pH adjustment as needed, to form a mixed metal precipitate. The mixed metal precipitate is added to the alumina slurry and the resulting solids are recovered by filtration, dried and calcined in a non-reducing atmosphere to prepare an oxide form of the catalyst.

Some catalysts are further impregnated prior to calcination with one or more Group I and/or Group II elements. A compound of the Group I or Group II element, for example potassium hydroxide, may be dissolved in water and impregnated onto the catalyst by incipient wetness. Typically water that is substantially free of dissolved metals, for example de-ionized water, may be used. Alternatively semiconductor grade water may be used to dissolve the compound of the Group I or Group II element in order to reduce the introduction of contaminating cations which may inhibit the catalyst.

The term "aqueous solution" includes not only a solution in which the solute is completely dissolved but also a slurry in which part or all of the solute is undissolved. The aqueous solution also includes acidic, neutral or basic solutions. For starting materials with limited solubility in a neutral aqueous solution, acid or base may be added to increase the amount of dissolved starting material. Dissolution of starting materials may also be aided by heating the aqueous solutions. Typically the aqueous solutions are heated from about 50 °C to about 90 °C.

The concentration of the starting materials in the aqueous solutions may vary broadly. Generally the amount of starting materials in the aqueous solution or slurry ranges from about 5 weight percent to about 60 weight percent of the total weight of the solution or slurry. Typically, the amount of starting material in the solution or slurry is about 10 weight percent to about 30 weight percent.

Typically deionized water is used to prepare the aqueous solutions or slurries. The use of deionized water aids in the reduction of contamination of the catalysts from water borne cations.

The present invention is a catalyst composition of a formula of $A_aB_bSb_cV_dAl_eO_x$, wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present. Preferred catalysts are those wherein a is from about 0.01 to about 0.1, b is from about 0.1 to about 1, c is from about 0.5 to about 3, e is from about 4 to about 7 and x is determined by the valence requirements of the elements present. More preferred catalysts are those wherein B is at least one element selected from the group consisting of zinc, nickel, cobalt, iron, bismuth and niobium.

One embodiment of the present invention is a catalyst composition of a formula consisting essentially of $A_aB_bSb_cV_dAl_eO_x$, wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present. Preferred catalysts are those wherein a is from about 0.01 to about 0.1, b is from about 0.1 to about 1, c is

from about 0.5 to about 3, e is from about 4 to about 7 and x is determined by the valence requirements of the elements present. More preferred catalysts are those wherein B is at least one element selected from the group consisting of zinc, nickel, cobalt, iron, bismuth and niobium.

5 Illustrative catalyst compositions encompassed by the claimed subject matter include, but are not limited to, the following examples:

$Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Ni_{0.3}Sb_{1.5}V_{1.0}Al_{6.1}$; $Ni_{0.3}Sb_{3.0}V_{1.0}Al_{6.1}$;
 $Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Fe_{0.3}Sb_{1.5}V_{1.0}Al_{6.1}$; $Fe_{0.3}Sb_{3.0}V_{1.0}Al_{6.1}$;
 10 $Zn_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Cd_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Co_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Nb_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Bi_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Ga_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Sn_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Cr_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Nb_{0.16}Fe_{0.17}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Cr_{0.16}Fe_{0.17}Sb_{0.5}V_{1.0}Al_{6.1}$; $K_{0.15}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $K_{0.3}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $K_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $K_{0.15}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Na_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 15 $Cs_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Mg_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Ba_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Na_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $K_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; $Cs_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$;
 $Mg_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$; and $Ba_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$.

20 The calcination temperature affects the selectivity and activity of the oxide catalyst. The selectivity and activity of the oxide catalysts decrease with increasing calcination temperature over the range from about 450 °C to about 950 °C. Suitable oxide catalysts were prepared using calcination temperatures below about 700 °C. Preferred calcination temperatures are from about 450 °C to about 650 °C.

25 The elevating temperature velocity or heat-up rate during calcination also affects catalyst properties such as phase composition, attrition resistance, surface area and particle size. Acceptable catalyst may be prepared with a heat-up rate of from about 5 °C to about 30 °C/minute. A preferred heat-up rate is from about 10 °C/minute to about 20 °C/minute. A more preferred heat up rate is from about 5 °C/minute to about 10 °C/minute. The heating rate may be varied to modify the surface area of the catalyst. Generally, the surface area of the catalyst decreases with
 30 increasing heating rate velocity.

The maximum calcination temperature also affects the morphological properties of the catalyst. The catalysts become less amorphous, i.e. more crystalline,

as the calcination temperature increases. Contrary to many known oxidative dehydrogenation catalysts which require crystallinity to achieve good activity and selectivity, the catalysts compositions of the present invention are active when they are substantially amorphous. Increasing the crystallinity by calcination at increased temperatures above about 700 °C reduces the activity and selectivity of the catalyst of this invention.

The maximum calcination temperature affects the surface area of the catalyst. For example, at a calcination temperature of 850 °C the surface area of the catalyst is about 30 m²/gm and at a calcination temperature of 950 °C the catalyst has a surface area of about 5 m²/gm. Calcination temperatures which result in the formation of oxide catalysts with surface areas of from about 130 m²/gm to about 150 m²/gm are preferred. Catalysts having surface areas deviating from this preferred range of surface areas demonstrate reduced selectivity.

CARRIER

The catalyst may be used with or without a support or carrier. For some applications, a supported catalyst may be preferred. The support may be an inorganic material including, but not limited to, silica, titania, silica-titania, and zirconia. Alumina based supports are not preferred since they contribute to the deactivation or reduced activity of the catalyst. The preferred catalyst support materials are ones which are substantially free of alumina or aluminum.

The support may be loaded with the catalyst to an extent of from about 0 weight percent to about 50 weight percent of the total weight of the support. The catalyst precursor or oxide catalyst is typically deposited on the surface of the support. Alternatively, the catalyst precursor or oxide catalyst may be co-precipitated with a support forming a composition in which the catalyst is substantially uniformly distributed within and on the support. Preferably, the catalyst precursor or oxide catalyst is deposited on the surface of the support and/or the surface of any pores present in the support.

The catalyst precursor, a non-oxidized mixed metal composition, may be formed by co-precipitation in a slurry containing the support to deposit the catalyst precursor directly on the support. The combined catalyst precursor and support may then be calcined to convert the catalyst precursor into the catalytically active oxide

form of the catalyst. Alternatively, the catalyst precursor may be prepared and converted to the catalytically active oxide form which may then be deposited on the support by conventional methods, for example by forming a slurry of the oxide catalyst and support followed by filtration or evaporation of the solvent.

PRESSURE

The oxidative dehydrogenation reaction may be conducted at atmospheric or superatmospheric pressures. Generally the reactor pressures will range from about 0.1 Mpa (atmospheric pressure) to about 0.2 MPa (about 2 atmospheres). Preferably the reactor pressure ranges from about 0.1 MPa to about 0.15MPa.

TEMPERATURE

The temperature for the oxidative dehydrogenation reaction will depend upon the compound being dehydrogenated and the desired level of conversion. The temperature for the oxidative dehydrogenation reaction generally ranges from about 350 °C to about 650 °C. A preferred temperature range is from about 350 °C to about 500 °C. The catalyst is active at a temperature as low as 300 °C. A more preferred temperature range is from about 350 °C to about 450 °C. A most preferred temperature range is from about 350 °C to about 400 °C. The preferred range for a particular catalyst composition may vary as observed in Tables 2 and 3. For instance, examples 20 and 27 show high selectivity at the relatively low temperature of 450 °C. Other examples, such as 16 and 17 show high selectivity at the relatively high temperature of 550 °C. The temperatures shown in Tables 2 and 3 are the maximum temperatures in the reactor.

CONTACT TIME

The preferred length of time during which the saturated compound contacts the catalyst is governed by many factors including the reactor temperature, the catalyst composition, and the nature of the compound undergoing reaction. The contact time generally ranges from about 0.1 to about 20 seconds. Contact times of 0.3 to 6 seconds are preferred. Contact times are generally determined empirically to provide an acceptable compromise between conversion of the starting material to product and selectivity in the production of the product.

Percent conversion of starting material = (moles of consumed starting material/moles of starting material fed to the reactor) X 100. Percent selectivity for

the desired product = (moles of desired product formed / moles of starting material consumed) X 100. Percent yield per pass of desired product = (moles of desired product formed / moles of starting material fed to the reactor) X 100.

The contact time may be adjusted by co-feeding a diluent, such as nitrogen, carbon dioxide or helium, with the organic compound that will be oxidatively dehydrogenated. The diluent may be any material that is a gas or vapor at the reactor temperature and pressure and which does not react with the organic compound starting material, the unsaturated organic compound product or the catalyst. The diluent may be present in concentrations of up to about 25 moles of diluent per mole of paraffin fed to the reactor. Typically the diluent concentration is from about 7.0 moles to about 10.0 moles per mole of paraffin.

OXYGEN TO OLEFIN RATIO

The amount of oxygen employed in the oxidative dehydrogenation process is determined by factors such as the particular compound being dehydrogenated, the number of hydrogen atoms being removed and the conversion level. Generally oxygen may be supplied to the reaction zone in an amount to provide a paraffin-to-oxygen molar ratio of from about 1/0.01 to about 1/10. Typically the molar ratio of paraffin to oxygen ranges from about 1/0.1 to about 1/1.

The molecular oxygen may be introduced with or without a diluent gas. Suitable diluent gases include, but are not limited to, nitrogen, steam and carbon dioxide. The diluent gas may be added in ratios up to about twenty-five moles of diluent per mole of organic compound feed. The diluent gas is typically used in sufficient quantities to aid in heat removal and to avoid the formation of an explosive gas mixture.

One embodiment according to the present invention is a process for the oxidative dehydrogenation of an organic compound which comprises contacting the compound having at least two adjacent carbon atoms bonded together and each carbon atom having at least one hydrogen atom and having from 2 to 20 carbon atoms in a vapor phase at a temperature of at least about 300 °C in the presence of oxygen with a catalyst comprising $A_aB_bSb_cV_dAl_eO_x$ wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to

0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present.

Another embodiment according to the present invention is a process for the oxidative dehydrogenation of an organic compound which comprises contacting the compound having at least two adjacent carbon atoms bonded together and each carbon atom having at least one hydrogen atom and having from 2 to 20 carbon atoms in a vapor phase at a temperature of at least about 300 °C in the presence of oxygen with a catalyst consisting essentially of $A_aB_bSb_cV_dAl_eO_x$ wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present.

REACTOR

The catalyst may be used in either a fixed bed or fluidized bed reactor by using conventional methods to form catalyst particles in the size appropriate for fixed bed or fluidized reactors. The fluidized bed reactor is useful for certain oxidative dehydrogenation reactions, for example propane to propene, which are exothermic. Fluidized bed reactors are sometimes preferred for exothermic reactions since the temperature may be controlled easier than in a fixed bed reactor.

The foregoing disclosure and description of the invention are illustrative and explanatory thereof, and various changes in the details of the illustrated apparatus and construction and method of operation may be made without departing from the spirit of the invention.

EXAMPLE 1

Preparation of Catalyst - $Sb_{0.5}V_{1.0}Al_{6.1}$

51.5 gm of $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 800 mL of deionized water and continuously stirred while 30% NH_4OH was added to adjust the pH to 7.5-8.0 to obtain white flocculent precipitate of alumina. A white slurry of 2.6 gm of $SbCl_3$ in 8 mL of 0.5 N HCl was added to a solution of 2.63 gm of NH_4VO_3 dissolved in 75 mL of hot deionized water forming a pale-brown suspension. The pH of the suspension was adjusted to 7.5-8.0 with 30% NH_4OH . Under stirring, the slurry obtained was

added to that previously prepared alumina slurry to obtain a homogenized mixture. The resulting product was obtained as a cake by filtration. The cake was dried at 120 °C for 5 hours. The cake was calcined by heating from 120 °C to 430 °C at a rate of 20 °C/minute and then maintained at 430 °C. The heat-up period from 120 °C to 430 °C and the period during which the cake was maintained at 430 °C totaled 4 hours. The temperature was then increased to 650 °C at 20 °C/minute. The heat-up period from 430 °C to 650 °C and the period during which the cake was maintained at 650 °C totaled 4.5 hours.

EXAMPLE 2

Preparation of Catalyst - $\text{Ni}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

103.0 gm of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 1600 mL of deionized water and continuously stirred while 30% NH_4OH was added to adjust the pH to 7.5 to obtain a gelatinous precipitate. Separately, 5.26 gm of NH_4VO_3 was dissolved in 150 mL of hot deionized water and a solution of 3.4 gm of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 mL of deionized H_2O was added to the NH_4VO_3 solution to obtain green-orange solution. A white slurry of 5.1 gm of SbCl_3 in 15 mL of 0.5 N HCl was added to the NH_4VO_3 solution forming a greenish-blue suspension. The pH of the mixture was adjusted by the addition of 30% NH_4OH to 7.5 and metallic gray precipitate was obtained. Under stirring, the resultant slurry was added to that previously prepared alumina slurry to obtain homogenized mixture. The resulting product was obtained as a cake by filtration. The cake was dried at 120 °C for 5 hours. The cake was calcined by heating from 120 °C to 430 °C at a rate of 20 °C/minute and then maintained at 430 °C. The heat-up period from 120 °C to 430 °C and the period during which the cake was maintained at 430 °C totaled 4 hours. The temperature was then increased to 650 °C at 20 °C/minute. The heat-up period from 430 °C to 650 °C and the period during which the cake was maintained at 650 °C totaled 4.5 hours.

EXAMPLE 3

Preparation of Catalyst - $\text{Ni}_{0.3}\text{Sb}_{1.5}\text{V}_{1.0}\text{Al}_{6.1}$

51.5 gm of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 800 mL of deionized water and continuously stirred while 30% NH_4OH was added to adjust the pH to 7.5 to obtain

white gelatinous precipitate. Separately, 2.6 gm of NH_4VO_3 was dissolved in 75 mL of hot deionized water. A solution of 1.8 gm of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 8 mL of deionized H_2O was added to the NH_4VO_3 solution to obtain orange-green suspension. Separately, a white slurry of 7.7 gm of SbCl_3 in 20 mL of 0.5 N HCl was added to $\text{NH}_4\text{VO}_3/\text{NiCl}_2$ suspension. The suspension pH was adjusted to 7.5-8.0 with 30% NH_4OH to obtain metallic gray mixture. Under stirring, the resultant slurry was added to that previously prepared alumina slurry to obtain homogenized mixture. The resulting product was obtained as a cake by filtration. The cake was dried at 120 °C for 5 hours. The cake was calcined by heating from 120 °C to 430 °C at a rate of 20 °C/minute and then maintained at 430 °C. The heat-up period from 120 °C to 430 °C and the period during which the cake was maintained at 430 °C totaled 4 hours. The temperature was then increased to 650 °C at 20 °C/minute. The heat-up period from 430 °C to 650 °C and the period during which the cake was maintained at 650 °C totaled 4.5 hours.

EXAMPLE 4

Preparation of Catalyst - $\text{Ni}_{0.3}\text{Sb}_{3.0}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 3 was used except 15.4 gm of SbCl_3 in 40 mL of 0.5 N HCl was used.

EXAMPLE 5

Preparation of Catalyst - $\text{Fe}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 2 was used except 6.1 gm of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 15 mL of deionized water was used instead of the nickel salt.

EXAMPLE 6

Preparation of Catalyst - $\text{Fe}_{0.3}\text{Sb}_{1.5}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 2 was used except 3.0 gm of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used instead of the nickel salt to produce an olive-green precipitate.

EXAMPLE 7

Preparation of Catalyst - $\text{Fe}_{0.3}\text{Sb}_{3.0}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure used in Example 3 was followed except 3.0 gm of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used instead of the nickel salt.

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EXAMPLES 8-10 and 12-14

Preparation of Catalyst - $\text{M}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$; where M = Zn, Cd, Co, Bi, Ga, Sn.

The following catalysts were synthesized according to Example 5, except $\text{Fe}(\text{NO}_3)_3$ was replaced by the metal salts listed in Table 1.

10

Table 1

Example Number	Metal Salts	Weight in gm.	Solvent (mL)	Final Color of Slurry
8	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.23	Water(15)	Metallic Grey
9	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.23	Water (15)	Grayish Green
10	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	1.34	Water(15)	Dark Green
12	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	3.60	23% HNO_3 (15)	Pale Orange
13	$\text{Ga}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	2.16	Water(15)	Metallic Grey
14	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	2.63	Water(15)	Metallic Grey

EXAMPLE 11

Preparation of Catalyst - $\text{Nb}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 2 was followed except 4.0 gm of NbCl_3 dissolved in 15 mL of concentrated HCl was used instead of the nickel salt in water.

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EXAMPLE 15

Preparation of Catalyst - $\text{Cr}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 2 was followed except 6.0 gm of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used instead of the nickel salt.

EXAMPLE 16

Preparation of Catalyst - $\text{Nb}_{0.16}\text{Fe}_{0.17}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

100.3 gm of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 1600 mL of deionized water and continuously stirred while 30% NH_4OH was added to adjust the pH to 7.5 to obtain a gelatinous precipitate. A solution of 3.0 gm of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 20 mL of deionized H_2O was added to a solution of 5.26 gm of NH_4VO_3 dissolved in 150 mL of hot deionized water to obtain an orange precipitate. A slurry of 5.1 gm of SbCl_3 and a slurry of 2.0 gm of NbCl_5 , each in 15 mL of 0.5 N HCl , were added to the $\text{NH}_4\text{VO}_3/\text{Fe}(\text{NO}_3)_3$ precipitate to form a pale brown suspension. The pH of the mixture was adjusted to 7.5 - 8.0 with 30% NH_4OH . The resultant slurry was added to the previously prepared alumina slurry to obtain a homogenized mixture. The resulting product was obtained as a cake by filtration. The cake was dried at 120 °C for 5 hours. The cake was calcined by heating from 120 °C to 430 °C at a rate of 20 °C/minute and then maintained at 430 °C. The heat-up period from 120 °C to 430 °C and the period during which the cake was maintained at 430 °C totaled 4 hours. The temperature was then increased to 650 °C at 20 °C/minute. The heat-up period from 430 °C to 650 °C and the period during which the cake was maintained at 650 °C totaled 4.5 hours.

EXAMPLE 5

Preparation of Catalyst - $\text{Cr}_{0.16}\text{Fe}_{0.17}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$

The procedure in Example 16 was followed except 6.0 gm of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in water was used instead of the niobium salt in HCl .

EXAMPLES 18-21

Preparation of Catalyst - $\text{K}_x\text{Fe}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$; where $x = 0.015$ (18); 0.03 (19); 0.06 (20); 0.15 (21)

The base material, $\text{Fe}_{0.3}\text{Sb}_{0.5}\text{V}_{1.0}\text{Al}_{6.1}$, was prepared by the procedure in Example 5 except that the base material was only calcined at 430 °C for 4.5 hours. Semiconductor grade KOH was dissolved in water and impregnated by incipient wetness onto the base material. The weight of KOH used was calcined according to the atomic ratios indicated in the formulas for each example. The resulting KOH

impregnated base material were dried at 120 °C for 5 hours. The product was then heated to 650 °C at a rate of 20 °C/minute. The heat-up period from 120 °C to 650 °C and the period during which the product was maintained at 650 °C totaled 4.5 hours.

EXAMPLES 22-25

Preparation of Catalyst - $M_{0.06}Fe_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$ where M = Na (22); Cs (23); Mg (24); Ba (25)

The procedure in Examples 18-21 was followed sodium hydroxide, cesium hydroxide, magnesium hydroxide, and barium hydroxide were respectively substituted for KOH. The weight of the Na, Cs, Mg and Ba hydroxides used were calculated according to the atomic ratios described in the formulas of Examples 22-25.

EXAMPLES 26-30

Preparation of Catalyst - $M_{0.06}Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$ where M = Na (26); K (27); Cs (28); Mg (29); Ba (30)

Base material $Ni_{0.3}Sb_{0.5}V_{1.0}Al_{6.1}$ was prepared by the procedure in Example 5 except the base material was only calcined at 430 °C for 4.5 hours. Sodium hydroxide, potassium hydroxide, cesium hydroxide, magnesium hydroxide, and barium hydroxide, respectively, were dissolved in water and impregnated onto the base material by incipient wetness. The weights of the Na, K, Cs, Mg and Ba hydroxides were calculated according to the atomic ratios described in the formulas of Example 26-30, respectively. The resulting metal hydroxide impregnated base material were dried at 120 °C for 5 hours. The product was then heated to 650 °C at a rate of 20 °C/minute. The heat-up period from 120 °C to 650 °C and the period during which the product was maintained at 650 °C totaled 4.5 hours.

Catalyst Testing Conditions

0.5 cc of catalyst prepared as described in Examples 1-30 was placed in a ¼ inch I.D. stainless steel fixed bed reactor. Propane, oxygen and helium were fed into the reactor, at the temperatures indicated in Tables 2 and 3, in the volume ratio of 2:1:17. The contact time was 0.3 seconds.

Table 2

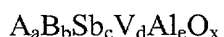
Example Number	Catalyst atomic Composition	Temperature (°C)	Conversion(%)		Selectivity to C ₃ H ₆ (%)
			C ₃ H ₈	O ₂	
1	Sb _{0.5} V _{1.0} Al _{6.1}	350	8.8	42.3	36.9
		450	19.9	90.6	34.1
		550	47.6	100	53.6
2	Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	6.4	43.5	45.5
		450	19.2	88.4	37.3
3	Ni _{0.3} Sb _{1.5} V _{1.0} Al _{6.1}	350	11.0	35.2	47.9
		450	21.6	100	30.1
4	Ni _{0.3} Sb _{3.0} V _{1.0} Al _{6.1}	350	9.4	24.7	47.5
		450	18.4	96.8	38.9
5	Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	5.3	19.8	64.3
		450	20.6	95.9	40.8
		550	40.0	100	38.3
6	Fe _{0.3} Sb _{1.5} V _{1.0} Al _{6.1}	350	10.7	40.6	40.3
		450	17.8	97.5	36.3
7	Fe _{0.3} Sb _{3.0} V _{1.0} Al _{6.1}	350	1.9	36.3	30.7
		450	15.8	100	34.6
8	Zn _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	5.2	25.7	55.6
		450	20.7	97.3	39.7
		550	41.5	100	49.4
9	Cd _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	3.7	28.3	46.4
		450	18	99.4	24.9
		550	33.7	100	36.9
10	Co _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	6.0	24.5	46.4
		450	19.1	99.5	31.3
		550	33.4	100	46.4
11	Nb _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	450	18.3	100	34.5
		550	46.3	100	55.4
12	Bi _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	4.0	11.1	61.8
		450	15.9	89.5	46.5
		550	24.0	100	42.7
13	Ga _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	9.7	45.9	38.5
		450	18.5	90.7	35.8
		550	47.1	100	52.4
14	Sn _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	14.6	65.8	32.9
		450	18.8	100	37.0
15	Cr _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	19.7	85.8	35.0
		450	29.3	100	38.3
		550	37.4	100	45.8
16	Nb _{0.16} Fe _{0.17} Sb _{0.5} V _{1.0} Al _{6.1}	450	18.2	100	41.6
		550	34.5	100	54.8
17	Cr _{0.16} Fe _{0.17} Sb _{0.5} V _{1.0} Al _{6.1}	450	19.7	100	38.8
		550	35.8	100	52.6

Table 3

Example Number	Catalyst atomic Composition	Temperature (°C)	Conversion(%)		Selectivity to C ₃ H ₆ (%)
			C ₃ H ₈	O ₂	
18	K _{0.15} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	3.5	15.0	65.3
		400	12.0	64.4	46.1
		450	20.0	100	45.2
19	K _{0.3} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	3.1	8.6	75.0
		400	10.2	39.8	56.2
		450	20.9	100	47.0
20	K _{0.06} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	2.1	5.8	85.7
		450	15.5	51.3	56.2
		550	23.7	100	42.9
21	K _{0.15} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	400	2.7	15.9	75.0
		450	5.5	30.9	66.7
22	Na _{0.06} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	8.6	47.1	43.3
		450	18.6	97.5	38.9
		550	32.6	100	54.3
23	Cs _{0.06} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	11.8	24.3	58.6
		450	24.0	100	41.3
24	Mg _{0.06} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	15.8	48.9	35.5
		450	26.4	100	27.8
		550	33.8	100	45.3
25	Ba _{0.06} Fe _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	15.4	45.3	39.1
		450	20.8	98.3	36.0
		550	25.3	100	40.0
26	Na _{0.06} Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	10.3	26.9	55.7
		450	22.3	100	41.5
27	K _{0.06} Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	2.2	5.1	88.1
		450	11.9	51.3	62.1
		550	32.3	100	49.0
28	Cs _{0.06} Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	9.2	26.7	57.5
		400	22.3	100	56.8
		550	35.0	100	55.5
29	Mg _{0.06} Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	11.2	30.1	51.4
		450	20.7	100	39.2
		550	34.6	100	55.0
30	Ba _{0.06} Ni _{0.3} Sb _{0.5} V _{1.0} Al _{6.1}	350	4.3	33.5	60.1
		450	19.3	93.6	56.8
		550	32.7	100	54.9

CLAIMS:

1 1. A catalyst composition for the oxidative dehydrogenation of a
2 compound having at least two adjacent carbons atoms bonded to one another and each
3 carbon atom having at least one hydrogen atom bonded thereto comprising



4
5 wherein A is an alkali or alkaline earth metal; B is one or more optional elements
6 selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium,
7 niobium, tin and neodymium; and a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3
8 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the
9 elements present.

1 2. The catalyst of claim 1, wherein the catalyst composition is of an
2 amorphous structure.

1 3. The catalyst of claim 1, having a surface area of from about 130 to
2 about 150 meters squared per gram.

1 4. The catalyst of claim 1, wherein the catalyst was produced at a
2 calcination temperature of from about 450 °C to about 650 °C.

1 5. The catalyst of claim 4, wherein to reach the calcination temperature
2 an elevating temperature velocity of about 20 °C per minute was utilized.

1 6. The catalyst of claim 1, wherein the catalyst composition is on a
2 support.

1 7. The catalyst of claim 6, wherein the support contains substantially no
2 aluminum.
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1 15. The method of claim 14, wherein to reach the calcination temperature
2 an elevating temperature velocity of about 20 °C per minute was utilized.

1 16. The method of claim 11, wherein the catalyst composition is on a
2 support.

1 17. The method of claim 16, wherein the support is silica, titania or
2 zirconia.

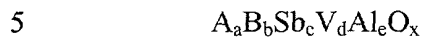
1 18. The method of claim 16, wherein the support contains substantially no
2 aluminum.

1 19. The method of claim 11, wherein a is from about 0.01 to about 0.1; b is
2 from about 0.1 to about 1; c is from about 0.5 to about 3; e is from about 4 to about 7;
3 and x is determined by the valence of the elements present.

1 20. The method of claim 11, wherein A is at least one of the elements
2 selected from the group consisting of potassium, cesium, magnesium and barium and
3 wherein B is at least one of the elements selected from the group consisting of zinc,
4 nickel, cobalt, iron, bismuth and niobium.

ABSTRACT

A catalyst composition for oxidative dehydrogenation of paraffinic hydrocarbons and other compounds having at least two adjacent carbon atoms each having at least one hydrogen atom. The catalyst composition is represented by the formula



wherein A is an alkali or alkaline earth metal; B is one or more optional elements selected from zinc, cadmium, lead, nickel, cobalt, iron, chromium, bismuth, gallium, niobium, tin and neodymium; a is 0 to 0.3, b is 0 to 5, c is 0.5 to 10, d is 1, e is 3 to 10, $7 \leq a+b+c+d+e \leq 25$, and x is determined by the valence requirements of the elements present. A process for the oxidative dehydrogenation of paraffins using the catalyst composition.

SOLE/JOINT INVENTOR
ORIGINAL/SUBSTITUTE/CIP**DECLARATION**

As a below named inventor, I hereby declare that: my residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first, and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

CATALYST SYSTEM FOR OXIDATIVE DEHYDROGENATION OF PARAFFINS

as described in the specification [X] attached or [] of patent Application Serial No. _____, filed _____ and amended on _____.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above; that I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application; that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representative or assigns more than twelve months prior to this application; and that I acknowledge the duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations § 1.56(a). Such information is material when it is not cumulative to information already of record or being made of record in the application, and

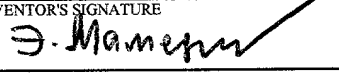
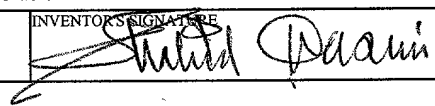
- (1) it establishes, by itself or in combination with other information, a prima facie case of unpatentability of a claim; or
(2) it refutes, or is inconsistent with, a position the applicant has taken or may take in:
(i) opposing an argument of unpatentability relied on by the Office, or
(ii) asserting an argument of patentability.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificates listed below and have also identified below any foreign application(s) having a filing date before that of the application(s) on which priority is claimed:

COUNTRY	APPLICATION NUMBER	DATE OF FILING	PRIORITY CLAIMED UNDER 35 USC 119
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

I hereby claim the benefit under Title 35 United States Code § 120 of any United States application(s) listed below and, insofar as any subject matter of any claim of this application is not disclosed in the prior United States Application, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations § 1.56(a) which occurred between the filing date of the prior application and the national PCT international filing date of this application: _____.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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